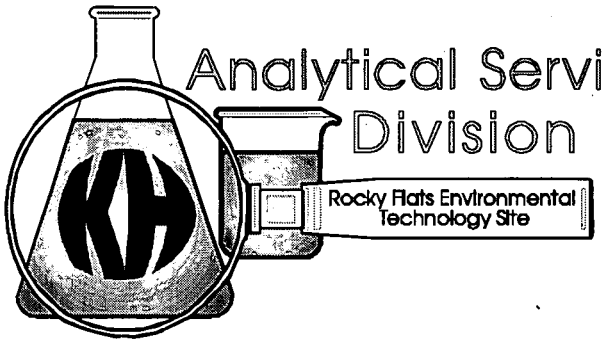



# VERIFICATION AND VALIDATION GUIDELINES

# FOR

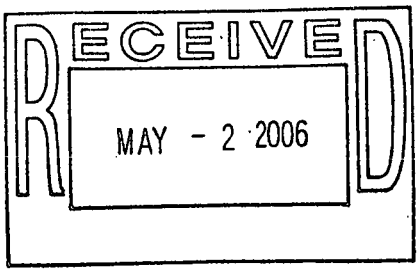
# WET CHEMISTRY PARAMETERS

# DA-SS06-v3

Effective Date: October 1, 2002

Approved: E A Brousky

Analytical Services Division




Reviewed For Classification
By: Roger S. Cichorz U/NU
ASD Project Lead – T130C
Date: June 4, 2002

ADMIN RECORD

SW-A-005431

1/35

## TABLE OF CONTENTS

# V & V GUIDELINE CHANGE DESCRIPTION FORM

| **Instructions:** Replace Version 2 with Version 3 |
|---|

| **Guideline:** DA-SS06 | **Version:** 3 | **Originator:** Shelly Johnsen |
|---|---|---|
| **Description:** Verification and Validation Guidelines For Wet Chemistry Parameters | | |

| Section No. | Change Description |
|---|---|
| N/A | Document Name change, new version and effective date. |
| Introduction | A new introduction was written to incorporate the BOA SOW rather than PSA Modules. |
| Entire Document | For clarity, change bars appearing on a Section Title indicate changes to the entire Section. |
| Entire Document | References to the BOA SOW and the RFETS BOA Implementation document GR03 & GR04, are incorporated throughout the document. References to PSA Modules were eliminated. References to Module Specific Verification and Validation (V & V) Guidelines were replaced with Analytical Specific V & V guidelines. |
| Data Review Checklist | All references to the Data Review Checklist and its examination were removed from the Guidelines. |
| Entire Document | All actions that involve Reason Codes 801, or 803 were revised to include an NCN be issued to request missing, incomplete data, or corrected data. The action requires the discontinuation of further assessment until corrected data is received and the action also requires a comment in the DQA Report identifying the request for missing or corrected data. |
| Entire Document | Ignitability, Corrosivity, Reactive Cyanide, and Reactive Sulfide were moved from DA-SS08 and incorporated into DA-SS06 |
| Section 2 | Expanded the scope of these guidelines to include analyses of all matrices. The previous title inferred the applicability was limited to aqueous samples only. |
| Section 2.3 | The entire section for Sample and QC Results was revised to include steps that meet BOA and GR03 requirements. The section was also reorganized to include data assessment steps for "Validation Only". |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |

## 1. PURPOSE AND INTRODUCTION

This document presents those data assessment steps which are unique to Wet Chemistry Parameter Analyses. This Analytical Specific document is to be used in conjunction with DA-GR01, "General Guidelines for data Verification and Validation.

The purpose of this document is to provide guidance in the completion of Data Verification, and Data Validation activities as part of the Rocky Flats Environmental Technology Site (RFETS) Analytical Services Division Data Assessment Process as described in DA-GR01.

This version of DA-SS06 is applicable to Wet Chemistry Parameter Data Packages generated under the National Basic Ordering Agreement (BOA) Statement of Work (SOW) and the Rocky Flats Environmental Technology Site (Site) BOA Implementation Requirements documents, GR03 & GR04.

## 2. VERIFICATION AND VALIDATION INSTRUCTIONS

The instructions contained in this section are specific to Wet Chemistry Parameter analyses for all sample matrices. They are to be used in conjunction with the general instructions for Verification and Validation found in Analytical Services Division's General Guidelines for Verification and Validation, DA-GR01.

### 2.1. Chain of Custody, Holding Times, and Sample Preservation

**Review Items:** COC, Laboratory Sample Receiving Documentation, Cover Page Comments, Sample Case Narrative, raw data, data summary forms, and sample preparation/extraction log.

**Objective:** The objective is to ascertain the validity of results based on the method required holding times, sample preservation, and the continuity of sample custody.

**Source:** BOA Attachment 1, § 3.1.2, and Base Method

***Evaluation:*** ***The following items apply to both verification and validation:***

**Item 1:** Determine if the samples were properly preserved prior to laboratory sample receipt using the criteria provided in Table 1.

***Action 1:*** If samples were not acid-preserved and/or were not maintained at 4° ±2° C prior to receipt by the laboratory, do not qualify the sample results. However, comment and assign the reason code **[703]** to all applicable samples.

**Item 2:** Check for documentation that the sample pH was adjusted to ≤ 2 or ≥ 12 by the laboratory if an aqueous sample was not adjusted to the proper pH prior to receipt by the laboratory.

***Action 2:*** If an aqueous sample was not adjusted to the proper pH by the laboratory, when required, issue a Non-Compliance Notification (NCN) and qualify all results as estimated **[ J 201]**.

**Item 3:** Determine if samples were properly preserved after sample receipt.

***Action 3:*** If documentation specifically indicates sample preservation was not maintained after sample receipt, but prior to analysis, issue a NCN requesting a corrective action to prevent recurrence and qualify all results as estimated **[J 201]**.

**Item 4:** Determine the actual analysis and preparation holding times by comparing the preparation and analysis dates on the raw data and the sample collection date on the COC. If the actual holding time is greater than the maximum allowable holding time per Table 1, qualify all results according to the following guidelines:

***Action 4a:*** Qualify all positive results when the actual holding time was greater than the maximum holding time but less than two-times the maximum holding time as follows:

- If the hold time violation is attributed to the lab issue a NCN and estimate **[J 101]** all applicable data.
- If the hold-time violation is not attributed to the laboratory, estimate **[J 701]** all applicable data.

***Action 4b:*** Qualify all non-detects as rejected (R) and detects as estimated (J) when the actual holding time was greater than two times the maximum holding time as follows:

- If the hold time violation is attributed to the lab, issue a NCN and assign qualifier **[R/J 102]**.
- If the hold-time violation is not attributed to the laboratory, assign qualifier **[R/J 702]**.

***Action 4c:*** Qualify all non-detects when the actual holding time was greater than the maximum holding time but less than two times the maximum holding time as follows:

- If the hold time violation is attributed to the lab, issue a NCN and assign the qualifier **[UJ 101]**.
- If the hold-time violation is not attributed to the laboratory, assign qualifier **[UJ 701]**.

**Table 1-HOLDING TIME AND PRESERVATION Criteria**

| Analyte | Holding Time (max.) | Preservation | |
|---|---|---|---|
| | | Aqueous Matrix | Non-Aqueous Matrix |
| Acidity | 14 days | Storage at 4°C | N/A |
| Alkalinity (Total as $CaCO_3$) | 14 days | Storage at 4°C | N/A |
| Alkalinity (Bicarbonate) | 14 days | Storage at 4°C | N/A |
| Alkalinity (Carbonate) | 14 days | Storage at 4°C | N/A |
| Ammonia as N | 28 days | pH<2 $H_2SO_4$, 4°C | N/A |
| BOD5 | 2 days | Storage at 4°C | N/A |
| Bromide | 28 days | Storage at 4°C | Storage at 4°C |

**Table 1-HOLDING TIME AND PRESERVATION CRITERIA (continued)**

| Analyte | Holding Time (max.) | Preservation | |
|---|---|---|---|
| | | Aqueous Matrix | Non-Aqueous Matrix |
| CBOD5 | 2 days | Storage at 4°C | N/A |
| COD | 28 days | pH<2 $H_2SO_4$, 4°C | N/A |
| Chloride | 28 days | Storage at 4°C | Storage at 4°C |
| Chromium IV | 24 hours | Storage at 4°C | Storage at 4°C |
| Cyanide, Total | 14 days | pH>12 NaOH, 4°C | Storage at 4°C |
| Cyanide, Total (RCRA) | 14 days | pH>12 NaOH, 4°C | Storage at 4°C |
| Cyanide, Amenable | 14 days | pH>12 NaOH, 4°C | Storage at 4°C |
| Cyanide, Amenable (RCRA) | 14 days | pH>12 NaOH, 4°C | Storage at 4°C |
| Cyanide, Releasable (RCRA) | 14 days | pH>12 NaOH, 4°C | Storage at 4°C |
| Fluoride | 28 days | Storage at 4°C | Storage at 4°C |
| Hardness, as $CaCO_3$ | 180 days | pH<2 $HNO_3$, 4°C | N/A |
| Nitrate as N | 48 hours | Storage at 4°C | Storage at 4°C |
| Nitrite as N | 48 hours | Storage at 4°C | Storage at 4°C |
| Nitrate/Nitrite as N | 28 days | pH<2 $H_2SO_4$, 4°C | N/A |
| Oil and Grease | 28 days | pH<2 $H_2SO_4$, 4°C | Storage at 4°C |
| DOC | 28 days | pH<2 $H_2SO_4$, 4°C | N/A |
| TOC | 28 days | pH<2 $H_2SO_4$, 4°C | N/A |
| pH | 24 hours | Storage at 4°C | Storage at 4°C |
| Phenol | 28 days | Storage at 4°C | Storage at 4°C |
| Phosphate (ortho) | 48 hours | Storage at 4°C | Storage at 4°C |
| Phosphate (total) | 28 days | pH<2 $H_2SO_4$, 4°C | N/A |
| Sediment Analysis | N/A | Storage at 4°C | N/A |
| Silica as $SiO_2$ | 28 days | Storage at 4°C | N/A |
| NVSS | 7 days | Storage at 4°C | N/A |
| Total Solids | 7 days | Storage at 4°C | N/A |
| TDS | 7 days | Storage at 4°C | N/A |
| TSS | 7 days | Storage at 4°C | N/A |
| Specific Conductance | 28 days | Storage at 4°C | N/A |
| Sulfate as $SO_4^{2-}$ | 28 days | Storage at 4°C | Storage at 4°C |
| Sulfide as $H_2S$ | 7 days | pH>9 NaOH, 4°C | Storage at 4°C |
| Sulfide as S | 28 days | Storage at 4°C | N/A |
| Total Kjeldahl Nitrogen (TKN) | 28 days | pH<2 $H_2SO_4$, 4°C | N/A |
| Total Organic Halides (TOX) | 7 days | pH<2 $H_2SO_4$, 4°C | N/A |
| Total Petroleum Hydrocarbons | 14 days | Storage at 4°C | N/A |
| Turbidity | 48 hours | Storage at 4°C | N/A |
| Ignitability | N/A | N/A | N/A |

**Table 1-HOLDING TIME AND PRESERVATION CRITERIA (continued)**

| Analyte | Holding Time (max.) | Preservation | |
|---|---|---|---|
| | | Aqueous Matrix | Non-Aqueous Matrix |
| Corrosivity (Aqueous Waste) | Analyze Immediately | Storage at 4°C | Storage at 4°C |
| Corrosivity (Liquid Waste) | Analyze Immediately | Storage at 4°C | Storage at 4°C |
| Reactive Cyanide | 14 days | pH>12 NaOH, 4°C | Storage at 4°C |
| Reactive Sulfide | 7 days | pH>12 Zinc Acetate, 4°C | Storage at 4°C |

## 2.2. Sample Data Package Narrative Requirements

**Review Item:** Sample Case Narrative

**Objective:** Review the narrative for compliance to requirements and for information useful to data assessment.

**Source:** GR03 § 3.2, BOA Attachment 1, § 3.1.6.2

***Evaluation:*** ***The following items apply to both verification and validation:***

**Item 1:** Check that the SDP Narrative is present and includes the following as applicable:

- Procedures and/or Standard Method reference for preparation and analysis.
- Descriptions of significant technical difficulties encountered in preparing and analyzing the samples.
- Justification of all dilutions.
- Explanations of any QC deficiencies, missed holding times, or inability to achieve the required detection limits (RDLs).
- Reasons for reanalysis, reanalysis Analytical Batch Identifications Numbers, and a synopsis of the reanalysis Analytical Batch QC Assessment.
- Explanations and descriptions of all deviations from routine protocols, including deviations from approved standard operating procedures (SOPs), detection limit modifications, etc. If it was necessary to contact the CTR for instructions due to the nature of the deviation, the laboratory shall document those instructions in the narrative.

***Action 1:*** If any of the above items are non-compliant, do not qualify the results, comment and include the reason codes **[227]** and/or **[805]** as appropriate. Use professional judgement to determine if the issuance of a NCN is warranted.

2.3. **Sample Results**

**Review Item:** Forms 1, 2, 3, 4, 5, and 6 or their equivalent

**Objective:** To confirm that sample results and qualifiers are correctly entered on the Form 1.

**Sources:** Attachment I to BOA Attachment 1, GR03 § 5, and Base Method

***Evaluation:*** ***The following items apply to both verification and validation:***

**Item 1:** Check that Form 1 is present for each sample in the Report Identification Number (RIN) and the Form 1 includes the Parameter Identifier for each requested analyte.

***Action 1:*** If forms are missing, issue a NCN, comment and assign reason code **[801]** to all applicable data. Inspect all other SDP deliverables for missing information and incorporate any deficiencies into the NCN. Discontinue the data assessment until a new data package is received.

**Item 2:** Check that one and only one result is reported on Forms 1 for each requested analyte.

***Action 2:*** If more than one result is reported and neither is identified as "Do Not Use data", issue a NCN, comment and assign reason code **[803]** to all applicable data. Inspect all other SDP deliverables for missing information and incorporate any deficiencies into the NCN. Discontinue the data assessment until a new data package is received.

**Item 3** Verify the following are compliant, complete, and without errors:

- Check that results for samples are reported in the same units as those used for the Required Detection Limits (RDL) provided in Attachment K to BOA Attachment 1 or in GR03.
- Check that results are reported to the correct number of significant figures. (**Note**: The concentration result shall be reported to 2 significant figures if the result is $< 10$; to 3 significant figures if the value is $\geq 10$. ).
- Check that the detection limit of each diluted sample (MDL * dilution factor) for a non-detected analyte is $\leq$ the specified RDL defined in the line item code
- Check that all qualifiers are entered correctly for each analyte.

  **Note:** A "U" is to be entered if the reported value is less than the MDL and a "B" if the result is greater than or equal to the MDL, but less than the RDL.

***Action 3a:*** Noncompliant items, omissions, or errors that do not have an impact on the assessor's ability to assess the data shall be documented with a comment and assigned the reason code **[804]**. An NCN shall be issued to prevent the recurrence of such errors or omissions in future data packages.

***Action 3b:*** For other noncompliant items, omissions or errors that impact the assessor's ability to complete the data review, issue a NCN, comment and assign reason

code **[803]** to all applicable data. Inspect all other SDP deliverables for missing information and incorporate any deficiencies into the NCN. Discontinue the data assessment until a new data package is received.

***Evaluation:*** ***The following Items apply validation only:***

**Item 4:** Examine the raw data to verify that the correct calculation was used to report the results of the summary Form 1 for each parameter listed on the COC record. Recalculate at least 3 sample parameter results from the raw data and verify the following are compliant, complete, and without errors:

- Check that results are reported without blank correction in the appropriate units as given in the line item code. Perform a blank correction check on at least one sample result for each method or LIC.
- Check that results for detected analytes are factored by all dilutions. Perform this check on at least one sample result for each method or LIC.
- Check that results for non-detected analytes are reported to the MDL and factored for any dilutions.

***Action 4:*** If reported results do not match raw data, issue a NCN, comment and assign reason code **[803]** to all applicable data. Inspect all other SDP deliverables for missing information and incorporate any deficiencies into the NCN. Discontinue the data assessment until a new data package is received.

## 2.4. Calibration Verification

**Review Items:** Wet Chem Form 2 or equivalent, Misc. Form 3 or equivalent, Mis. Form 4 or equivalent, preparation logs, standard logs, instrument logs, instrument printouts, and raw data.

**Objective:** To determine that all analytical results were obtained from instrumentation that was in calibration according to the analytical method. Initial calibration verification (ICV) is performed to provide assurance of the accuracy of the calibration standards. The analysis of continuing calibration verification standards (CCV) establishes that the initial calibration is still valid by checking the performance of the instrument on a continual basis. Sources of standards used for calibration and ICV/CCV must be independent. If these sources are truly independent and ICV/CCV results meet the evaluation criteria, then the probability of gross calibration error is small.

**Sources:** BOA Attachment 1, § 3.2.3; Attachment I to BOA Attachment 1, GR03 § 5, and Base Method

***Evaluation:*** ***The following items apply to both verification and validation:***

**Item 1:** Check that Form 2, Form 3, or Form 4 are present and include results for *found* and *true* values.

**Note:** The Forms or their equivalents must be completed for all applicable analytes or all requested parameters except those determined by gravimetric methods and BOD/CBOD.

*Action 1:* If a required Form is missing, issue a NCN, comment and assign reason code **[801]** to all applicable data. Inspect all other SDP deliverables for missing information and incorporate any deficiencies into the NCN. Discontinue the data assessment until a new data package is received.

**Item 2:** Check that ICV/CCV results and %R values are reported for all applicable analytes.

*Action 2:* If ICV or CCV results are not reported for an analyte, issue a NCN and qualify all results for the analyte as rejected **[R 129]**.

***The following Item does not apply to pH/Corrosivity, Conductivity or Ignitability***

**Item 3:** Verify that all ICV/CCV percent recoveries (%R) are within the limits of 85 to 115% established in GR03.

*Action 3:* If the ICV/CCV %R for any parameter falls outside the acceptance windows, check for reanalysis of the affected samples bracketed by ICV/CCV analyses with %R values that are within the acceptance window. If any reported data is Not bracketed by acceptable calibration verifications (ICV or CCV), issue a NCN and qualify all affected data according to the following guidelines:

- If the ICV or CCV %R falls within the range of 70 to 84%, qualify all affected results as estimated **[J 104]**.
- If the ICV or CCV %R falls within the range of 116 to 130%, qualify all results greater than the MDL as estimated **[J 104]** results less than MDL are considered valid **[104]**.
- If the ICV or CCV %R is less than 70%, qualify all affected results as rejected **[R 104]**.
- If the ICV or CCV %R is greater than 130%, qualify all affected results greater than the MDL as rejected **[R 104]**.

**Note:** The ICV and CCV shall be analyzed in the same fashion as an actual sample. Operations such as the number of replicate analysis, the number and duration of the instrument rinses, etc. affect the measured ICV or CCV result and must not be applied to the ICV or CCV in a greater extent than they are applied to the associated analytical samples.

***The following is specific to Conductivity***

**Item 4:** Verify that all ICV/CCV (calibration check) percent recoveries (%R) are within the limits of 95 to 105% established in the base method.

*Action 4:* If the calibration check %R for conductivity falls outside the acceptance window, issue a NCN and qualify all data, not bracketed by acceptable calibration check for conductivity, according to the following guidelines:

- If the calibration check %R falls within the range of 85 to 94% or 106 to 115%, qualify all affected results as estimated **[J 104]**.
- If the calibration check %R is less than 85% or greater than 115%, qualify all affected results as rejected **[R 104]**.

***The following is specific to pH/Corrosivity***

**Item 5:** Verify that the Difference between the found and true values is within 0.1 S.U.

*Action 5:* If the Difference for pH/Corrosivity falls outside the acceptance window, issue a NCN and qualify all data from the analytical batch for pH/Corrosivity as estimated **[J 104]**.

***The following is specific to Ignitability***

**Item 6:** Verify that the *Difference* value of the Found and True values for the ICV and CCV standard are within the following acceptable limits:

- Ignitability Methods 1010 and 1020A: 27.2 ± 0.8° C for p-xylene

**Note:** If the *Difference* value for a ICV/CCV falls outside the acceptance windows, check for reanalysis of the affected samples bracketed by ICV/CCV analyses with *Difference* values that are within the acceptable limits.

*Action 6:* If any reported data is Not bracketed by acceptable calibration verifications (ICV or CCV), comment and qualify all data, not bracketed by acceptable calibration verifications for that parameter, according to the following guidelines:

- If either the ICV or CCV *Difference* for Ignitability falls outside the acceptable limits, comment and qualify at a minimum all data from the analytical batch as estimated **[J 104]**.

***The following is specific to BOD/CBOD***

**Item 7:** Verify that the correlation coefficient is ≥ 0.95.

*Action 7:* If the correlation coefficient is less than 0.95, qualify data as follows:

- If the correlation coefficient is less than 0.95 qualify all associated results as estimated **[J 153]**.
- If the correlation coefficient for BOD/CBOD is less than 0.95, estimate **[J 153]** all applicable data.
- If the slope is positive for BOD/CBOD, estimate **[J 153]** all applicable data.
- If the y-intercept is greater than the DO blank for BOD/CBOD estimate **[J 153]** all applicable data.

***Evaluation:*** ***The following item applies to validation only:***

***<u>The Following Items Apply to ICV/CCV Type Analyses</u>***

ICV/CCV requirements are applicable to colorimetric/ spectrophotometric, IC, IR, potentiometric (ISE), titrimetric, TOX, and turbidimetric techniques.

**Item 8:** Verify that an ICV was analyzed at the beginning of each analytical sequence following the calibration standards and before the analysis of site samples and the Initial Calibration Blank (ICB).

***Action 8:*** If an ICV was not analyzed or site samples were analyzed before the ICV, issue a NCN and qualify all samples analyzed before the first calibration verification sample as rejected **[R 129]**.

**Item 9:** Verify that a CCV standard was analyzed after the last analytical sample.

***Action 9:*** If a CCV was not analyzed after the last site samples were analyzed, issue a NCN and qualify all samples analyzed after the last acceptable CCV as rejected **[R 129]**.

**Item 10:** Verify that no more than 20 samples were analyzed between the analyses of the ICV and the first CCV (include all samples analyzed except ICBs, and CCVs). Check that no more than 20 samples were analyzed between any two consecutive analyses of the CCV (include all samples analyzed except CCBs and CCVs).

**Action 10:** If more than 20 samples were analyzed between any calibration verification standards, comment and assign the reason code **[129]** to all samples analyzed within this calibration verification bracket.

***<u>The following applies to ICV/CCV type analyses with a %R value:</u>***

**Item 11:** Compare the ICV/CCV results and subsequent % R values for 3 of each of the parameters from the raw data to the results reported on the summary forms. If one or more of the raw data results do not agree with results reported on the summary form to 2 significant figures or the %R value does not agree to within 1 decimal place, check all reported ICV/CCV results and %R values against the raw data.

***Action 11:*** If the raw data and reported data do not agree, issue a NCN, comment and assign reason code **[803]** to all applicable data. Inspect all other SDP deliverables for missing information and incorporate any deficiencies into the NCN. Discontinue the data assessment until a new data package is received.

***The Following Items Apply to Gravimetric Measurements:***

The laboratory shall provide the analytical balance standardization verification results for the balance check weight measurements (ICV/CCV) prior to analytical batch measurements. The standardization verifications shall meet all requirements of GR03 5.2.5.2.

**Item 12:** Check the raw data for documentation showing balance check weight measurements were performed on the day(s) the gravimetric determination was performed.

*Action 12:* If balance standardization calibration verifications are not present, issue a NCN, comment and assign reason code **[801]** to all applicable data. Inspect all other SDP deliverables for missing information and incorporate any deficiencies into the NCN. Discontinue the data assessment until a new data package is received.

**Item 13:** Check the raw data for documentation of acceptable gravimetric verification measurements (ICV/CCV) or check weight measurements prior to analytical batch measurements.

*Action 13:* If balance standardization calibration verifications were not acceptable, estimate **[J 104]** all applicable data.

***The Following Item Applies to Ion Chromatography Analysis:***

**Item 14:** Check any IC raw data for documentation that the response or retention times for any sample or standard IC analyte does not vary from calibration standards by more than 10%. Check for reanalysis of samples having deviant retention times with diluted samples.

*Action 14:* If the retention time for any reported analyte varies by more than 10%, issue a NCN and reject **[R 234]** all applicable data.

***The Following Item Applies to Titrimetric, pH/Corrosivity and Conductimetric Analyses:***

**Item 15:** Check titrimetric, pH/Corrosivity, and conductimetric raw data to verify that standardizations were conducted and documented.

*Action 15:* If the appropriate standardization was not completed, comment and assign reason code **[106]**.

***The Following Item Applies to Ignitability:***

**Item 16:** Verify that an ICV was analyzed at the beginning of each analytical sequence following the calibration standards and before the analysis of site samples.

*Action 16:* If an ICV was not analyzed or site samples were analyzed before the ICV, reject **[R 129]** all samples analyzed before the first calibration verification sample.

**Item 17:** Verify that a CCV standard was analyzed after the last analytical sample.

*Action 17:* If a CCV was not analyzed or site samples were analyzed before the CCV, reject **[R 129]** all samples analyzed before the first calibration verification sample.

**Item 18:** Verify that no more than 10 samples were analyzed between the analyses of the ICV and the first CCV (include all samples analyzed except ICBs, and CCVs). Check that no more than 10 samples were analyzed between any two consecutive analyses of the CCV (include all samples analyzed except CCBs and CCVs).

*Action 18:* If more than 10 samples were analyzed between any calibration verification standards, comment and assign the reason code **[129]** to all samples analyzed within this calibration verification bracket.

**Item 19:** Verify from the instrument raw data that the *Difference* for at least two calibration verification samples are comparable to those reported on Form 3. If one or more of the raw data results do not agree with results reported on Form 3 to two significant figures, all reported ICV and CCV results must be checked against raw data.

*Action 19:* If one or more of the raw data results do not agree with results reported on Form 3 to two significant figures, issue a NCN, comment and assign reason code **[803]** to all applicable data. Inspect all other SDP deliverables for missing information and incorporate any deficiencies into the NCN. Discontinue the data assessment until a new data package is received.

***The Following Items Apply to Methods that Utilize a Calibration Line:***

**Item 20:** Verify that the minimum number of standards at the required concentration levels and at the required frequency were used to calibrate the instrument upon use according to the appropriate base method specified in the Line Item Code.

*Action 20:* If the minimum number of standards were not used or the instrument was not calibrated at the appropriate frequency, issue a NCN and reject **[R 106]** all applicable data.

**Item 21:** Verify that the correlation coefficient for each applicable method is $\geq$ 0.995.

*Action 21:* If the correlation coefficient is less than 0.995, issue a Non-Compliance-Notification and qualify all associated results as estimated **[J 103]**.

2.5. **Blanks**

**Review Items:** Wet Chem Form 3 or equivalent, Misc. Form 4 or equivalent, instrument logs, instrument printouts, and raw data.

**Objective:** To determine the existence and magnitude of contamination resulting from preparation and analysis activities. Blanks may be assessed to establish potential false positive results attributable to variances in instrument operating conditions or due to contamination introduced into the analytical system.

**Sources:** Attachment I to BOA Attachment 1, GR03 § 5, and Base Method

***Evaluation:*** ***The following items apply to both verification and validation:***

***<u>The Following Items Apply to Methods that Require an ICB/CCB and PB:</u>***

ICB/CCB requirements are applicable to colorimetric/spectrophotometric, IC, IR, potentiometric (ISE), titrimetric, TOX, and turbidimetric techniques. Preparation blanks are required for all methods and for each analytical batch.

**Note:** A BOD/CBOD dilution water blank must be processed with each BOD/CBOD batch and the DO uptake reported as the PB result.

**Item 1:** Check that Form 3s or Form 4s are present for each method used and results reported for each analyte requested.

*Action 1:* If Form 3s or Form 4 are not provided, issue a NCN, comment and assign reason code **[801]** to all applicable data. Inspect all other SDP deliverables for missing information and incorporate any deficiencies into the NCN. Discontinue the data assessment until a new data package is received.

**Item 2:** Verify that Form 3 Blank results are reported to the MDLs.

*Action 2:* If the Form 3 results are not reported appropriately, issue a NCN, comment and assign reason code **[803]** to all applicable data. Inspect all other SDP deliverables for missing information and incorporate any deficiencies into the NCN. Discontinue the data assessment until a new data package is received.

**Item 3:** Verify that the MDL for each analyte is equal to or less than the RDL listed in Attachment K to Attachment 1 of the BOA.

*Action 3:* If the MDL is greater than the RDL, issue a NCN and qualify all non-detected results as rejected **[R 213]**.

**Item 4:** Verify that the absolute value of any ICB, CCB, or PB result is not greater than the MDL and RDL for any parameter. Check for the reanalysis of all samples associated with unacceptable blanks, if applicable.

*Action 4a:* Sample results for an analyte that are greater than 10 times the absolute value of the blank result may be accepted without qualification.

**Note 1:** The analysis should be terminated when the absolute value of any blank result exceeds the RDL.

**Note 2:** GR03 states that if the PB concentration is greater than the RDL, all associated samples with analyte concentrations less than five times the blank concentration shall be redigested and reanalyzed for that analyte as part of a new complete analytical batch.

*Action 4b:* If any blank result is greater than the RDL, qualify sample results as follows:

- Qualify all non-detected sample results as valid but assign reason code **[159]**.
- Qualify all positive results less than 5X the absolute value of the blank result as rejected **[R 159]**.
- Qualify all positive results ≤10X and ≥5X of the absolute value of the blank result as estimated **[J 159]**.

*Action 4c:* If any blank result is less than the negative RDL, qualify sample results as follows:

- Qualify all sample results less than the MDL and all detected results less than 5X the absolute value of the blank result as rejected **[R 159]**.

*Action 4d:* If any blank result is between the negative MDL and the negative RDL then,

- Qualify all sample results with non-detects as estimated **[J 107]**.
- Qualify all positive results less than 5X the absolute value of the blank result as estimated **[J 107]**.

*Action 4e:* If any blank result is greater than the positive MDL but less than the RDL,

- All sample results less than the MDL are accepted without qualification.
- Qualify all positive results less than 5X the blank result as estimated **[UJ 107]**.

*Evaluation:* ***The following items apply to validation only:***

***<u>The Following Items Apply to Methods that Require an ICB/CCB and PB:</u>***

**Item 5:** Compare the ICB/CCB and PB results for 3 of each of the parameters from the raw data to the results reported on the summary forms.

*Action 5:* If the raw data and reported data do not agree, issue a NCN, comment and assign reason code **[803]** to all applicable data. Inspect all other SDP deliverables for missing information and incorporate any deficiencies into the NCN. Discontinue the data assessment until a new data package is received.

**Item 6:** Check that the initial calibration blank (ICB) is analyzed after the analytical standards but not before analysis of the ICV, during the initial calibration of the instrument.

*Action 6:* If the ICB is not analyzed in the proper order, comment and assign the reason code **[129]**.

**Item 7:** Check that the final CCB standard was analyzed after the last CCV was analyzed.

*Action 7:* If the final CCB was not analyzed after the final CCV, comment and assign the reason code **[129]**.

**Item 8:** Check that no more than 20 solutions were analyzed between any two consecutive analyses of CCB (include all solutions analyzed except ICVs/ICBs and CCVs/CCBs).

*Action 8:* If more than 20 solutions were analyzed between calibration verification samples, comment and assign the reason code **[129]** to all affected samples.

**Note:** Calibration blanks are to be analyzed in the same fashion as an actual sample. Operations such as the number of replicate analysis, the number and duration of the instrument rinses, affect the measured blank result and are not to be applied to the blank in a greater extent than they are applied to the associated analytical samples.

**Item 9:** Check the raw data to verify that one PB was processed for each analytical batch.

*Action 9a:* If no PB was processed when required, issue a NCN and qualify results ≤10 (RDL) as rejected **[R 230]**.

*Action 9b:* If no PB was processed when required, issue a Non-Compliance Notification and qualify results >10(RDL) as estimated **[J 230]**.

***The Following Item Applies to BOD/CBOD PB (dilution water blank):***

GR03 requires that a BOD/CBOD dilution water blank is processed with each BOD/CBOD batch and the DO uptake reported as a PB result. If BOD/CBOD analyses are performed by Standard Methods and the DO uptake is more than 0.2 mg/L, the results should be qualified. However, BOD/CBOD analyses must be performed by the HACH Method given in GR03, and the HACH Graphical calculation method automatically compensates for the DO uptake of the dilution water and seed.

**Item 10:** Check that the Y intercept of each sample and standard BOD/CBOD plot agrees with the final measured dissolved oxygen value of the incubated seed blank or dilution water blank to within ± 0.5 mg/L.

*Action 10:* If the Y intercept of a sample plot does not agree with the final seed blank or dilution water blank DO value to within ± 0.5 mg/L, estimated **[J 149]** all applicable data.

## 2.6. Matrix Spike Analysis

**Review Items:** Wet Chem Form 4 or equivalent, Misc. Form 4 or equivalent, and raw data.

**Objective:** To assess the impact of matrix effects on the sample analytical results. Analysis of spiked samples provides information about the effect of each sample matrix on the sample preparation procedures and the measurement methodology.

**Sources:** Attachment I to BOA Attachment 1, GR03 § 5, and Base Method

***Evaluation:*** ***The following items apply to both verification and validation:***

***The Following Applies to all Applicable Methods Requiring a* Matrix Spike Analyses**

The frequency of preparation and analysis of matrix spikes must meet all requirements of base methods. At a minimum, one matrix spike is required in each analytical batch for colorimetric/spectrophotometric, IC, IR, potentiometric (ISE), titrimetric, TOX, and turbidimetric techniques.

**Item 1:** Check that at least one Form 4 is present for each method, matrix, waste type, and analytical batch with the % R, correct control limits, and reported in the same units as sample results.

*Action 1:* If Form 4s are not provided, issue a NCN, comment and assign reason code **[801]** to all applicable data. Inspect all other SDP deliverables for missing information and incorporate any deficiencies into the NCN. Discontinue the data assessment until a new data package is received.

**Item 2:** Determine if one matrix spike was analyzed for each matrix or waste type within an analytical batch of 20 or fewer field samples.

*Action 2a:* If a matrix spike was not analyzed at the proper frequency, issue a NCN and estimate **[J 168]** all applicable data.

*Action 2b:* If no matrix spike was analyzed, regardless of frequency, issue a NCN for the missing QC and estimate **[J 230]** all applicable data.

**Item 3:** Determine if the control limits of 75% to 125% are correctly assigned (as applicable).

*Action 3:* If the control limits are not assigned correctly, comment and assign the reason code **[232]** to all applicable data. Continue to evaluate spike results using the correct limits.

**Item 4:** Determine if a "N" flag is applied when warranted.

*Action 4:* If a "N Flag" is not present when required, comment and assign reason code **[804]** to all applicable data.

**Item 5:** Determine if matrix spike recoveries are within 75% to 125%.

*Action 5:* If spike recoveries are outside control limits, qualify data as follows:

- If the spike recovery is >125% and the reported sample results are < MDL, the data are valid.
- If the spike recovery is within125 to 150% and the sample result is >(MDL), the data are estimated **[J 112]**.
- If the spike recovery is greater than 150% and the sample result is >(MDL), the data are rejected **[R 112]**.
- If the spike recovery is within the range of 50 to 74%, all sample results are estimated **[J 112]**.
- If the spike recovery is less than 50%, all results are rejected **[R 113]**.

**Note 1:** Spike recovery criteria do not apply when the sample result for an analyte is >4 times the spike level.

***Evaluation:*** ***The following items apply to validation only:***

***The Following Applies to all Applicable Methods Requiring a* Matrix Spike Analyses**

**Item 6:** Check that a spiked sample was subjected to the same sample preparation, dilution, analytical methods, and QA/QC procedures employed for the Site samples.

***Action 6:*** If a matrix spike was not prepared and analyzed in the same manner as the Site samples, issue a NCN and estimated **[J 168]** all applicable data.

**Item 7:** Check that no samples identified as blanks were used for spiked sample analysis.

***Action 7:*** If a matrix spike was prepared using a sample identified as a blank sample, issue a NCN and estimate **[J 168]** all applicable data.

**Item 8:** Check the spike concentration levels were equivalent to the mid-point concentration level of the calibration curve. Samples requiring preparation and subsequent dilution for analysis are exempted.

***Action 8:*** If a matrix spike was completed with incorrect spike concentration level, comment and assign reason code **[234]**.

**Note:** For methods not requiring preparation before analysis, spikes may be added to samples after necessary dilutions have been performed, however the spiked and unspiked sample dilution levels must be identical.

**Item 9:** Compare the matrix spike results and subsequent % R values for 3 of each of the parameters from the raw data to the results reported on the summary forms. If one or more of the raw data results do not agree with results reported on the summary form to 2 significant figures or the %R value does not agree to within 1 decimal place, check all reported matrix spike results and %R values against the raw data.

***Action 9:*** If the raw data and reported data do not agree, issue a NCN, comment and assign reason code **[803]** to all applicable data. Inspect all other SDP

deliverables for missing information and incorporate any deficiencies into the NCN. Discontinue the data assessment until a new data package is received.

**Item 10:** Recalculate from the raw data one or more of the spiked sample percent recoveries (%R) using the following equation and verify that the recalculated value agrees with the laboratory reported value on Form 4 to within 0.1%. If the results cannot be verified, recalculate all spike recoveries.

$$\%R = (SSR-SR) \times 100 / SA$$

Where:

SSR = Spiked Sample Result
SR = Sample Result (see note)
SA = Spike Added

**Note:** When the sample concentration is less than the method detection level (MDL), use SR=0 only for the purposes of calculating the %R.

*Action 10:* If the %R values do not compare, issue a NCN, comment and assign reason code **[803]** to all applicable data. Inspect all other SDP deliverables for missing information and incorporate any deficiencies into the NCN. Discontinue the data assessment until a new data package is received.

## 2.7. Laboratory Duplicate Analysis

**Review Items:** Wet Chem Form 5 or equivalent, Misc. Form 4 or equivalent, and raw data.

**Objective:** To verify acceptable precision of sample results for the sample matrix, laboratory preparation, and analysis procedure. Duplicate sample determinations are used to measure variability due to a combination of factors including laboratory precision, method precision, and sample homogeneity.

**Sources:** Attachment I to BOA Attachment 1, GR03 § 5, and Base Method

*Evaluation:* ***The following items apply to both verification and validation:***

***Replicate Spiked Sample Verses Duplicate Sample***

If a replicate spiked sample is analyzed instead of a duplicate sample then the spike and spiked replicate are reported on Form 5. Use the same evaluation rules, substituting measured spiked sample values for the sample concentrations.

**Item 1:** Check that Form 5s or Form 4s are present for each parameter, matrix, waste type, and analytical batch at the required frequency.

*Action 1:* If the Form 5s or Form 4s are not available, issue a NCN, comment and assign reason code **[801]** to all applicable data. Inspect all other SDP deliverables for missing information and incorporate any deficiencies into the NCN. Discontinue the data assessment until a new data package is received.

**Item 2:** Verify that the Relative Percent Difference (RPD) **control limits** for each analyte are assigned correctly.

***The Following Criteria Applies to Wet Chemistry Methods Except pH/Corrosivity and Conductivity***

- If both the original and duplicate sample values are <(MDL), the control limit column was left blank (No value should have been entered in the RPD column on the Form 5 or the RPD column should have been left blank for this analyte).
- If both the original and duplicate sample values are ≥(5) * (RDL), the value of 20% was entered in the "Control Limit" column.
- If either one or both of the original and duplicate values is <(5)(RDL) and ≥RDL, the RDL was entered as the limit in the "Control Limit" column of Form 5.

***The following Criterion Applies to pH/Corrosivity and Conductivity***

- Verify that the control limit for a pH/Corrosivity result is entered as 0.1 S.U. and the control limit for a conductivity result is entered as 5%.

*Action 2:* If the control limits are not assigned correctly, comment and assign the reason code **[232]**. Continue to evaluate duplicate results using the correct limits.

**Item 3:** Complete the following checks for the subsequent RPD of the original and duplicate results of each requested analyte to determine if the **RPD result** is entered correctly on the Form per the following:

***The Following Criteria Applies to Wet Chemistry Methods Except pH/Corrosivity, Conductivity, and Sand Silt Split***

- If the original and duplicate sample values are <(MDL), the RPD column was left blank.
- If both the original and duplicate sample values are ≥(5)(RDL), the RPD was entered in the Form 5 RPD column.
- If either one or both of the original and duplicate values is <(5)(RDL) and ≥RDL, the absolute *Difference* was entered in the Form 5 RPD column.

***The following Criterion Applies to pH/Corrosivity***

- For pH/Corrosivity, the absolute value of the *Difference* between the sample and duplicate sample results was entered to one decimal place.

***The following Criterion Applies to Conductivity, and Sand Silt Split***

- For conductivity and sand silt split, the *RPD* between the sample and duplicate sample results was entered to one decimal place.

*Action 3:* If the RPD column on the Form 5 was not completed correctly, issue a NCN, comment and assign reason code **[803]** to all applicable data. Inspect all other SDP deliverables for missing information and incorporate any deficiencies into the NCN. Discontinue the data assessment until a new data package is received.

**Item 4:** Determine if there was a reanalysis of samples associated with unacceptable lab duplicates. If a reanalysis was not performed, qualify data as follows:

***The Following Actions Apply to Wet Chemistry Methods Except pH/Corrosivity, Conductivity, and Sand Silt Split***

*Action 4a:* If the original and duplicate results are ≥(5)(RDL) and the *RPD* is greater than 20%, estimate **[J 111]** all applicable data.

*Action 4b:* If the original or duplicate result is <(5)(RDL) and >(RDL); the *Difference* between the duplicate and original sample is greater than the RDL, estimate **[J 111]** all applicable data.

***The following Action Applies to pH/Corrosivity***

*Action 4c:* If the absolute *Difference* between the original and duplicate results for pH/Corrosivity is greater than 0.1 S.U., estimate **[J 111]** all applicable data.

***The following Action Applies to Conductivity***

*Action 4d:* If the *RPD* between the original and duplicate results for conductivity is greater than 5%, estimate **[J 111]** all applicable data.

***If sufficient sample volume was provided, the following action applies to Sand Silt Split***

*Action 4e:* If the *RPD* between the original and duplicate results for sand silt split is greater than 20%, estimate **[J 111]** all applicable data.

***The following Action Applies to Applicable Wet Chemistry Methods***

**Item 5:** Check that the original and duplicate results corrected for any dilutions are present in the same units as reported on Form 1 to three significant figures.

*Action 5:* If original and duplicate results are not reported for a required WQP, issue a NCN and qualify all associated results as **[J 230]**.

***The following Item Applies to Ignitability***

**Note:** Duplicate data for ignitability is not required since 2 replicates are required for each sample. Therefore, no duplicate data is required for Form 3. The following item is assessed against the sample replicate.

**Item 6:** Verify that the absolute value of the *Difference* for ignitability results is reported in the narrative if the replicate absolute *Difference* value is greater than 5° C.

***Action 6:*** If the ignitability replicate *Difference* value is outside of the criteria, estimate **[J 111]** the sample result.

***Evaluation:*** ***The following items apply to validation only:***

**Item 7:** Check that a duplicate sample was subjected to the same sample preparation, analytical methods, and QA/QC procedures employed for the Site samples.

***Action 7:*** If a duplicate was not prepared and analyzed in the same manner as the Site samples, issue a NCN and estimate **[J 168]** all applicable data.

**Item 8:** Check that no samples identified as blanks were used for duplicate sample analysis.

***Action 8:*** If a duplicate was prepared using a sample identified as a blank sample, issue a NCN and estimate **[J 168]** all applicable data.

***The Following Item Applies to Wet Chemistry Methods Except pH/Corrosivity***

**Item 9:** Check the raw data (instrument printouts, strip charts, bench sheets) to verify that the original and duplicate results corrected for any dilutions and subsequent *RPD* results on Form 5 were accurately transcribed to within 2 significant figures for the results and 0.1% for the *RPD* value.

Recalculate from the raw data one or more of the RPD values using the following equation:

$$RPD = \frac{|S - D|}{(S + D)/2} 100$$

Where:

RPD = Relative Percent Difference
S = First Sample Value (original sample)
D = Second Sample Value (duplicate)

***Action 9:*** If the %R values do not compare, issue a NCN, comment and assign reason code **[803]** to all applicable data. Inspect all other SDP deliverables for missing information and incorporate any deficiencies into the NCN. Discontinue the data assessment until a new data package is received.

***The Following Item Applies to pH/Corrosivity***

**Item 10:** Check the raw data for pH/Corrosivity (instrument printouts, strip charts, bench sheets) to verify that the original and duplicate results and subsequent *Difference* results on Form 5 were accurately transcribed to within 2 significant figures for the results and 1 decimal place for the *Difference* value.

Recalculate from the raw data one or more of the *Difference* values using the following equation:

$$Difference = |S - D|$$

***Action 10:*** If the raw data and reported data do not agree or the *Difference* values do not compare, issue a NCN, comment and assign reason code **[803]** to all applicable data. Inspect all other SDP deliverables for missing information and incorporate any deficiencies into the NCN. Discontinue the data assessment until a new data package is received.

***The Following Item Applies to Ignitability***

**Item 11:** Check the raw data (instrument printouts, strip charts, bench sheets) to verify that the average of 2 replicate results on Form 1 was accurately transcribed to within 2 significant figures for the results.

Recalculate from the raw data one or more of the *Difference* values using the following equation:

$$Difference = |S - D|$$

***Action 11:*** If the raw data and reported data do not agree, issue a NCN, comment and assign reason code **[803]** to all applicable data. Inspect all other SDP deliverables for missing information and incorporate any deficiencies into the NCN. Discontinue the data assessment until a new data package is received.

## 2.8. Laboratory Control Sample Analysis

**Review Items:** Form 6 or equivalent and raw data.

**Objective:** To determine the overall laboratory performance of each step from preparation through analysis.

**Sources:** Attachment I to BOA Attachment 1, GR03 § 5, and Base Method

***Evaluation:*** ***The following items apply to both verification and validation:***

For methods not requiring preparation before analysis, an LCS is to be added to the analytical batch and analyzed as a sample. Regardless of whether sample preparation is required, and LCS is to be analyzed with each analytical method and parameter.

**Item 1:** Check that Form 6s are present and that results are reported for all requested analysis with the exception of ignitability.

*Action 1a:* If the Form 6s are not present, issue a NCN, comment and assign reason code **[801]** to all applicable data. Inspect all other SDP deliverables for missing information and incorporate any deficiencies into the NCN. Discontinue the data assessment until a new data package is received.

**Note:** LCS material may not be present for some matrices or waste types. The Case Narrative must explain that an equivalent or alternative matrix was used with CTR approval. However, regardless of whether sample preparation is required, an LCS is to be analyzed with each analytical batch for each analytical method and parameter.

*Action 1b:* If an LCS with the incorrect matrix was used, issue a NCN and estimate **[J 230]** all applicable data.

*Action 1c:* If an LCS was present but not at the appropriate frequency, issue a NCN and estimate **[J 168]** all applicable data.

*Action 1d:* If an LCS was not reported for an analyte, issue a NCN and estimate **[J 230]** all applicable data.

**Item 2:** Check that LCS results are within the control limits according to the following criteria:

- For all analytes except pH/Corrosivity, conductivity, and BOD/CBOD: the percent recovery (%R) must be within ±20% of the True Value.
- For pH/Corrosivity: the absolute value of the difference between the found and true LCS values must be ≤ 0.1 S.U.
- For conductivity: the percent recovery (%R) must be within ±5% of the True Value.
- For BOD/CBOD: the percent recovery (%R) must be within ±18% of the True Value.

*Action 2:* If there was no reanalysis of samples associated with unacceptable LCS results and the LCS results are not within the applicable control limits (see the following Note), qualify all associated sample results for each analyte according to the following criteria:

**Note:** If the %R for an LCS is not within the control limits, GR03 requires the analysis to be terminated, the problem corrected, the analytical batch to be reprepared, if necessary, and the reanalysis of the analytical batch.

- If the LCS recovery falls outside of the acceptance criteria but within 2 times the upper or lower control limit, qualify results > MDL, if applicable, as estimated **[J 110]**.
- If the LCS recovery is greater than 2 times the upper control limit, qualify results > MDL, if applicable, as rejected **[R 110]**.
- If the LCS recovery is greater than the upper acceptance limit, qualify results < MDL, if applicable, as valid **[V 110]**.
- If the LCS recovery falls below the lower limit but within 2 times the lower control limit, qualify all results <MDL, as estimated **[J 110]**.

- If the LCS recovery is less than 2 times the lower control limit, qualify all results, as rejected**[R 110]**.

***Evaluation:*** ***The following items apply to validation only:***

**Item 3:** Check that the LCS sample was subjected to the same sample preparation, analytical methods, and QA/QC procedures employed for the Site samples.

***Action 3:*** If a the LCS was not prepared and analyzed in the same manner as the Site samples, issue a NCN and estimate **[J 168]** all applicable data.

**Item 4:** Check that the LCS analyte concentration of each requested analyte is within the range of the analyte calibration curve.

***Action 4:*** If an LCS concentration was not within the calibration, comment and apply reason code **[234]** to all applicable data.

**Item 5:** Check the LCS raw data (instrument printouts, strip charts, bench sheets) to verify that the reported results and recoveries on Form 6 were accurately transcribed to within 0.1units (i.e., % or S.U.).

***Action 5:*** If the raw data and reported data do no agree, issue a NCN, comment and assign reason code **[803]** to all applicable data. Inspect all other SDP deliverables for missing information and incorporate any deficiencies into the NCN. Discontinue the data assessment until a new data package is received.

**Item 6:** Recalculate one or more of the reported percent recoveries (%R) for each parameter according to the following equation:

$$\%R = (\text{Found LCS Value} / \text{Expected LCS Value})100$$

Where:

| | | |
|---|---|---|
| Found LCS Value | = | Actual LCS result from laboratory analysis |
| Expected LCS Value | = | Expected LCS result based on certificate of analysis or equivalent record |

For pH/Corrosivity, recalculate from the raw data one or more of the difference values using the following equation:

$$Difference = |S - D|$$

Verify that the recalculated value agrees with the laboratory reported value on Form 6 to within 0.1 units (i.e., % or S.U.). If the results cannot be verified, recalculate all LCS values.

***Action 6:*** If the %R or *Difference* values do not compare, issue a NCN, comment and assign reason code **[803]** to all applicable data. Inspect all other SDP deliverables for missing information and incorporate any deficiencies into the NCN. Discontinue the data assessment until a new data package is received.

2.9. **Distillation Recovery Check for Reactivity**

**Review Items:** Misc. Form 4, and raw data.

**Objective:** To determine the overall laboratory performance of the distillation process.

**Sources:** Attachment I to BOA Attachment 1, GR03 § 5, and Base Method

***Evaluation:*** ***The following items apply to both verification and validation:***

**Item 1:** Check that a *Distillation Recovery Check* %R value is reported for each cyanide and sulfide analytical batch.

***Action 1:*** If a *Distillation Recovery Check* %R value is not present, reject **[R 230]** all applicable data.

**Item 2:** Check that the *Distillation Recovery Check* %R value is within the upper and lower control limits. Check for reanalysis of the analytical batch if the *Distillation Recovery Check* is not within the upper and lower control limits.

***Action 2:*** If the *Distillation Recovery Check* is not within the upper and lower control limits for either Reactivity method for the reported sample results, reject **[R 230]** all applicable data.

***Evaluation:*** ***The following items apply to validation only:***

**Item 3:** Verify that the upper and lower control limits for the *Distillation Recovery Checks* were determined and assigned according the following:

- The upper control limit for the Distillation Recovery Check is the *Mean Distillation Recovery* plus three times *Distillation Recovery Standard Deviation.*
- The lower control limit for the Distillation Recovery Check is the *Mean Distillation Recovery* minus three times the *Distillation Recovery Standard Deviation.*

***Action 3a:*** If the upper and lower control limits for the *Distillation Recovery Checks* were not determined to the above criteria, reject **[R 230]** all applicable data.

***Action 3b:*** If the upper and lower control limits for the *Distillation Recovery Checks* were not reported, issue a NCN, comment and assign reason code **[801]** to all applicable data. Inspect all other SDP deliverables for missing information and incorporate any deficiencies into the NCN. Discontinue the data assessment until a new data package is received.

**Item 4:** Check the raw data (strip charts, bench sheets) to verify that the reported *Distillation Recovery Checks* percent recoveries (%R) on Form 4 were accurately transcribed.

***Action 4:*** If the raw data and reported data do not agree, issue a NCN, comment and assign reason code **[803]** to all applicable data. Inspect all other SDP deliverables for missing information and incorporate any deficiencies into

the NCN. Discontinue the data assessment until a new data package is received.

**Item 5:** Recalculate from the raw data one or more of the *%R* values using the following equation:

%R = (Found Value / Expected Value)100

Where:

Found Value = Actual result from laboratory analysis

Expected Value = Certificate of analysis result or equivalent record

***Action 5:*** If the calculated %R values do not compare to within 0.1 % of the reported value, issue a NCN, comment and assign reason code **[803]** to all applicable data. Inspect all other SDP deliverables for missing information and incorporate any deficiencies into the NCN. Discontinue the data assessment until a new data package is received.

## 2.10. Corrosivity Toward Steel

**Review Items:** Misc. Form 5, and raw data.

**Objective:** To verify acceptable precision of sample results for the sample matrix, laboratory preparation, and analysis procedure.

**Sources:** Attachment I to BOA Attachment 1, GR03 § 5, and Base Method

***Evaluation:*** ***The following items apply to both verification and validation:***

**Item 1:** Check that a Misc. Form 5 or equivalent is present for each analytical batch and all reported samples in the RIN.

***Action 1:*** If a Form 5 is missing, issue a NCN, comment and assign reason code **[801]** to all applicable data. Inspect all other SDP deliverables for missing information and incorporate any deficiencies into the NCN. Discontinue the data assessment until a new data package is received.

**Item 2:** Check that each Form 5 is labeled with the Lab name, Lab Code, *Analytical Batch Identifier* and the RIN.

***Action 2:*** If the Form 5 Header is non-compliant, issue a NCN, comment and assign the reason code **[804]**.

**Item 3:** Verify that two replicate analyses were performed for each sample.

***Action 3:*** If at least two replicate analyses were not completed for each sample, comment and qualify the sample result as estimated **[J 168]**.

**Item 4:** Verify that the average of two replicate results was reported in the *Average* column of the Form 5 and the value agrees with the value reported on Form 1.

***Action 4a:*** If the average of two replicate results was not reported in the *Average* column of the Form 5 , comment and assign the reason code **[804]**.

*Action 4b:* If the Form 5 average result does not agree with the Form 1 reported result, issue a NCN, comment and assign reason code **[803]** to all applicable data. Inspect all other SDP deliverables for missing information and incorporate any deficiencies into the NCN. Discontinue the data assessment until a new data package is received.

**Item 5:** Verify that the control limits for Corrosivity Method 1110 are assigned according to the following criteria:

- If either R1 or R2 is greater than or equal to 20% of the regulatory limit (6.35 mm per year), the control limit is 20.0%.
- If both R1 and R2 are less than 20% of the regulatory limit, no Control Limit is required and no entry is needed in the Control Limit cell.

*Action 5:* If the control limits are not assigned correctly, comment and assign the reason code **[232]**. Continue to evaluate duplicate results using the correct limits.

**Item 6:** If the result reported in the *RPD* column is greater than the acceptable control limit, verify that the RPD of the replicate analyses is reported in the *RPD* column and that "*" Flags are present. Check for reanalysis of two additional replicates, if the RPD of the two original replicate results is greater than 20% and one of the results is greater than 20% of the regulatory limit for Corrosivity. Also, if the reanalysis RPD is greater than 20%, check that the results of the two highest replicates and subsequent RPD are reported.

**Note:** If reanalysis of replicates is required, the narrative must comment on both sets of data and include results for all four replicate analyses.

*Action 6:* If the RPD of replicate results for Corrosivity toward Steel is outside of the criteria, estimate **[J 130]** all applicable data.

*Evaluation:* ***The following items apply to validation only:***

**Item 7:** Check that the replicate analyses were subjected to the same sample preparation, analytical methods, and QA/QC procedures.

*Action 7:* If a replicate was not prepared and analyzed in the same manner as the other replicates, estimate **[J 168]** all applicable data.

**Item 8:** Check the raw data (instrument printouts, strip charts, bench sheets) to verify that the replicate results and subsequent *RPD* values on Form 5 were accurately transcribed to within 2 significant figures for the results and 0.1% for the *RPD* value.

*Action 8:* If the raw data and reported data do not agree issue a NCN, comment and assign reason code **[803]** to all applicable data. Inspect all other SDP deliverables for missing information and incorporate any deficiencies into the NCN. Discontinue the data assessment until a new data package is received.

**Item 9:** Recalculate from the raw data one or more of the *RPD* values using the following equation:

$$RPD = \frac{|R_1 - R_2|}{(R_1 + R_2)/2} 100$$

Where:

*RPD* = Relative Percent Difference

*R1* = *First Sample Value (replicate 1)*

*R2* = *Second Sample Value (replicate 2)*

***Action 9:*** If the calculated *RPD* value(s) do not compare to within 0.1% of the reported value, issue a NCN, comment and assign reason code **[803]** to all applicable data. Inspect all other SDP deliverables for missing information and incorporate any deficiencies into the NCN. Discontinue the data assessment until a new data package is received.

## 2.11. Sample Preparation and Analysis Methods

**Review Items:** Cover Page, COC, Case Narrative, Raw Data

**Objective:** To determine if the proper preparation and analysis methods were performed according to the Line Item Code, analyte, and sample matrix.

**Sources:** Attachment I to BOA Attachment 1, GR03 § 5, and Base Method

***Evaluation:*** ***The following Items apply to both verification and validation:***

**Item 1:** Compare the sample preparation and analysis procedures reported in the narrative and/or Cover Page to the appropriate method identified in Attachment I to BOA Attachment 1 or GR03 Section 5 for each Line Item Code requested.

***Action 1:*** If an incorrect method was used for sample preparation or analysis and a CTR approved deviation was not documented, issue a NCN and estimate **[J 207]** all applicable data.

***Evaluation:*** ***The following items apply to validation only:***

**Item 2:** Compare the sample preparation and analysis procedures listed on the preparation and analysis raw data to the appropriate methods identified in Attachment I to BOA Attachment 1 or GR03 Section 5 for each Line Item Code requested.

- If an incorrect method was used for sample preparation or analysis and a CTR approved deviation was not documented, issue a NCN and estimate **[J 207]** all applicable data.

2.12. **Sample Preparation Raw Data**

**Review Items:** Raw Data

**Objective:** To check that sample preparation raw data deliverable requirements have been met and that raw data are present in a form suitable for data assessment.

**Sources:** Attachment I to BOA Attachment 1, GR03 § 5, and Base Method

***Evaluation:*** ***The following items apply to validation only:***

**Item 1:** Check that preparation raw data (benchsheets and/or preparation logs) are included for all analyses performed and include the following:

- Analytical Batch Identifier
- date of preparation
- identifiers for all samples, sample duplicates, and spikes
- identifiers for at least one preparation blank and lab control sample
- at least one sample from each matrix type in the batch was run in duplicate and spiked
- samples are clearly linked to an associated spiked sample, lab duplicate sample, lab control sample, and preparation blank
- no digestion batch exceeds 20 analytical samples
- at least one set of duplicates, spikes, PBs, and LCSs for each analytical batch
- for aqueous samples initial and final volumes for all samples and QC samples
- for solids and non-aqueous liquids reported by weight, initial weights and final volumes for all samples and QC samples
- for samples reported by weight, balance identifiers with dates of use.
- dated signatures for at least one analyst and one reviewer

***Action 1a:*** Omissions or errors that do not have an impact on the assessor's ability to assess the data shall be documented with a comment and assigned the reason code **[804].** An NCN shall be issued to prevent the recurrence of such errors or omissions in future data packages.

***Action 1b:*** For other omissions or errors that impact the assessor's ability to complete the data review, issue a NCN, comment and assign reason code **[803]** to all applicable data. Inspect all other SDP deliverables for missing information and incorporate any deficiencies into the NCN. Discontinue the data assessment until a new data package is received.

**Item 2:** Check that sufficient raw data are included in the SDP to allow manual calculations of the final reported sample results.

***Action 2a:*** Omissions or errors that do not have an impact on the assessor's ability to assess the data shall be documented with a comment and assigned the reason code **[804]**. An NCN shall be issued to prevent the recurrence of such errors or omissions in future data packages.

*Action 2b:* For other omissions or errors that impact the assessor's ability to complete the data review, issue a NCN, comment and assign reason code **[803]** to all applicable data. Inspect all other SDP deliverables for missing information and incorporate any deficiencies into the NCN. Discontinue the data assessment until a new data package is received.

2.13. **Instrument Raw Data**

**Review Items:** Raw Data

**Objective:** To verify that the instrument raw data is provided for all reported data and that the data is consistent with the results reported on the summary forms.

**Source :** Attachment I to BOA Attachment 1, and Base Method

***Evaluation:*** ***The following items apply to validation only:***

**Item 1:** Check that instrument raw data are included for all analyses by performing the following checks:

- Check that all instrument raw data for the RIN are included and legible.
- Check at least one instrument printout or benchsheet for correctly identified spiked samples, if applicable, and laboratory duplicates.
- Check that instrument identifiers are on raw data, if applicable.
- Check at least ten raw data sheets, if available, for legibility and proper error correction techniques.
- Check that preparation blank and LCS data are clearly linked to the preparation batch.
- Check instrument raw data printouts or benchsheets for area chemist review, signature, and date on each instrument batch.
- Check this item as complete if raw data were sufficient to perform calculations for all previous items.
- Check that the batch QC was prepared in the same manner as the samples.

*Action 1a:* Omissions or errors that do not have an impact on the assessor's ability to assess the data shall be documented with a comment and assigned the reason code **[804]**. An NCN shall be issued to prevent the recurrence of such errors or omissions in future data packages.

*Action 1b:* For other omissions or errors that impact the assessor's ability to complete the data review, issue a NCN, comment and assign reason code **[803]** to all applicable data. Inspect all other SDP deliverables for missing information and incorporate any deficiencies into the NCN. Discontinue the data assessment until a new data package is received.

## 3. QUALITY ASSESSMENT REPORT PREPARATION

Prepare a Data Quality Assessment Report according to the General Data Assessment guidelines presented in DA-GR01. A Data Quality Assessment Report template for DV-SS06 is presented as Attachment 1.

## 4. REFERENCES


- USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review, February 1994.
- Reason Codes for Data Assessment, Analytical Services Document
- RFETS BOA Implementation Requirements, GR03 Version A.5
- RFETS BOA Implementation Requirements, GR04 Version A
- Basic Ordering Agreement (BOA) for Laboratory Analytical Services administered by Westinghouse Savannah River Company on behalf of the Department of Energy.

# ATTACHMENT 1: DATA QUALITY ASSESSMENT REPORT TEMPLATE

## WCH

## Data Quality Assessment Report

## Rocky Flats Environmental Technology Site

| RIN Number | Analytical Method/Analytical Specific Line Item Code | | Review Level |
|---|---|---|---|
| | | | |
| **Analytical Laboratory** | **Assessment Performed by** | **Data Assessment Guideline Identifiers** | **Number of Samples** |
| | | | |

Sample Numbers: _____

_____

| Quality Control Items | Reviewed (Y or N) | Non-Compliance Identified |
|---|---|---|
| General (Cover Page, Narrative) | | |
| Chain of Custody, Preservation, and Holdings | | |
| Sample Results | | |
| Calibration Verification, CRDL Standard | | |
| Verification and Preparation Blanks | | |
| Matrix Spike | | |
| Duplicates | | |
| Laboratory Control Sample | | |
| Method Detection Limits | | |
| Preparation and Analysis Methods | | |
| Preparation and Instrument RAW Data | | |
| EDD | | |
| Other: | | |

Y Item was reviewed or non-compliance was identified
N Item was not reviewed or non-compliance was not identified
N/A Item is not applicable to the Line Item

# WCH
# Data Quality Assessment Report
# Rocky Flats Environmental Technology Site

*Data Assessment results are classified as either Action Items or Comments. Action Items are technical non-compliances that result in qualification of analytical results. Data may be qualified as valid (V), estimated (J), presumptively estimated (NJ), estimated at an elevated level of detection (UJ), or rejected ( R). Multiple qualifiers may be associated with any given data point based on the number of problems identified, however, the assigned qualifier is based upon the following hierarchy: R, UJ, NJ, J, V. All data points that are not qualified based upon action items in this report are considered valid (V). Comments are technical non-compliances or contractual non-compliances that do not result in qualification of data.*

**Action Items:**

**Comments:**

Verification/Validation Signature_____ Date:_____

Reviewer Signature_____ Date:_____

(*Validation Only*)



35/35